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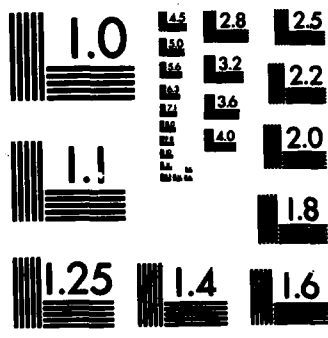
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MRL-TN-464

**SEPARATION OF NITRATION BY-PRODUCTS IN COMMERCIAL-GRADE
TRINITRO-TOLUENE BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY**

Peter J. Sanders

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ABSTRACT

Mixtures of several isomeric mononitro-, dinitro- and trinitro-toluenes were made up in toluene and analysed by HPLC techniques using reverse-phase, silica and amine columns and a variety of eluting solvents. A separation achieved on the silica column using dichloromethane/n-heptane as eluent under optimum conditions indicated that it could be used as a basis for further work in the analysis of production grade trinitro-toluene (TNT).

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Mixtures of several isomeric mononitro-, dinitro- and trinitro-toluenes were made up in toluene and analysed by HPLC techniques using reverse-phase, silica and amine columns and a variety of eluting solvents. A separation achieved on the silica column using dichloromethane/n-heptane as eluent under optimum conditions indicated that it could be used as a basis for further work in the analysis of production grade trinitro-toluene (TNT).

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SEPARATION OF NITRATION BY-PRODUCTS IN COMMERCIAL-GRADE
TRINITRO-TOLUENE BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

1. INTRODUCTION

For some time, a need has existed for the estimation of various nitro-toluenes formed in the production of commercial-grade 2,4,6-TNT.

Methods have been reported [1,2] for the separation and analysis of these isomers by gas-liquid chromatography (GLC), but it has been found that, even in the best of these GLC methods, accurate analyses of some of the nitro-toluene isomers present at the level of 0.01% cannot be obtained in production TNT samples. In these samples, the 2,4,6-TNT grossly overloads the column when using sample sizes required to give chromatographic peaks large enough for accurate analysis of these isomers.

In this paper, results from the application of isocratic High Performance Liquid Chromatography (HPLC) using different columns and different solvent mixtures are reported.

2. EXPERIMENTAL

2.1 Materials

A synthetic stock solution containing 0.5% each of five dinitro-toluenes (DNT's) and five trinitro-toluenes (TNT's) plus 4-mononitro-toluene (4-MNT) in toluene was made up from materials supplied by R.P. Parker and M.A. Parry of Explosives Research Group, Materials Research Laboratories, Maribyrnong.

2.2 Solvents

The eluting solvents used were Ajax Chemicals "Unichrom" HPLC grade solvents filtered through a 0.5 micrometer Millipore filter and degassed under vacuum. The toluene was a redistilled analytical reagent grade.

2.3 Instrument

The high performance liquid chromatograph (HPLC) used was a Hewlett Packard (H.P.) model 1081b, fitted with the H.P. 254 nm dual-beam ultra-violet absorption detector. This detector was used only in the single-beam mode, however, using air as the reference, and was set to the range 1.024 absorbance full-scale deflection. Also fitted was the H.P. variable volume auto-injector and a pellicular silica guard column. The column compartment was temperature controlled at 35°C throughout all work.

Electrical output from the HPLC was attached to a H.P. 5840 gas chromatograph in order to make use of its terminal.

2.4 Columns

Columns used were:-

Alltech 10 micron Silica	250 mm x 4.6 mm I.D.
Alltech 10 micron C18 Reverse-Phase	250 mm x 4.6 mm I.D.
Excalibar 10 micron Lichrosorb Amine	250 mm x 4.6 mm I.D.

These were prepared for use by flushing first with methanol then with propan-2-ol, they were then preconditioned to a stable baseline with the eluting solvent currently in use.

When dichloromethane was a component of the eluent, the columns were flushed out with propan-2-ol on completion of a day's experiments. When work was to recommence, the columns were then re-flushed with propan-2-ol then reconditioned to a stable baseline with the eluent currently in use.

2.5 Typical Eluents

(1) Dichloromethane/n-heptane	(10% : 90% V/V)
(2) Propane-2-ol/n-heptane	(0.25% : 99.75% V/V)
(3) Ethyl Acetate/n-heptane	(2.5% : 97.5% V/V)

2.6 Procedure

A working solution was prepared by diluting a quantity of the stock

solution 100:1 with toluene. For each run, 5.0 microlitres of this working solution were injected onto the column. Optimum conditions for the best resolution of the components for each column using various eluents were investigated during repeated elutions.

3. RESULTS

3.1 Reverse-Phase Column

It was found that the nitro-toluenes under investigation had so little affinity for this column material that they all eluted off with the toluene component even when using eluting solvents of the lowest possible polarity (such as 100% n-heptane).

3.2 Amine Column

This column failed to resolve the eleven component mixture to more than five peaks with dichloromethane/n-heptane eluent. In addition, several components eluted with the 2,4,6-TNT component.

3.3 Silica Column

When eluent (3) was used with this column, two components eluted with the 2,4,6-TNT peak and not all of the other components were resolved (Fig. 1). With eluent (2), resolution of all components still was not achieved (Fig. 2) but a relatively large separation was obtained between elution of the 2,4,6-TNT component and that immediately following. All components of the working solution were resolved to a greater or lesser extent when eluent (3) was used with the silica column, (Fig. 3). Five repeated runs were performed with this combination to obtain standard deviation in retention volumes, (Table 1).

4. CONCLUSIONS

An analytical technique could probably be based on the separative capabilities of the silica column with dichloromethane/n-heptane eluent. Ethyl acetate/n-heptane eluent has the advantage that it does not require flushing out at the end of each day's work, but, in this case, it did not achieve sufficient resolution.

The isomeric resolution could be greatly improved if a large part of the 2,4,6-TNT could be removed prior to analysis. This removal may be able to be achieved by stream-switching the effluent resulting from a separation on a silica column using propan-2-ol/n-heptane eluent, where there is a relatively large separation between 2,4,6-TNT and the following peak.

5. REFERENCES

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3. Alm, A., Dalman, O., Frolen-Lindgren, I., Hulten, F., Karlsson, T. and Kowalska, M. (1978). "Analyses of Explosives". FOA Report C 20267-D1, National Defence Research Institute, Department 2, Stockholm.

TABLE 1

Retention volume data for a synthetic mixture of eleven nitrotoluenes on an Alltech Silica Column 25 using 10% v/v dichloromethane/90% n-heptane eluent at 3.0 ml/min and 35°C.

COMPONENT	AVERAGE RETENTION VOLUME	PERCENT STANDARD DEVIATION
4-MNT	7.85 ml	2%
2,6-DNT	13.7 ml	3%
2,5-DNT	14.9 ml	3%
3,5-DNT	15.6 ml	3%
3,4-DNT	17.1 ml	3%
2,4-DNT	18.1 ml	2%
2,4,6-TNT	24.1 ml	3%
2,3,6-TNT	25.8 ml	2%
2,3,5-TNT	27.9 ml	3%
2,4,5-TNT	33.1 ml	2%
2,3,4-TNT	40.4 ml	2%

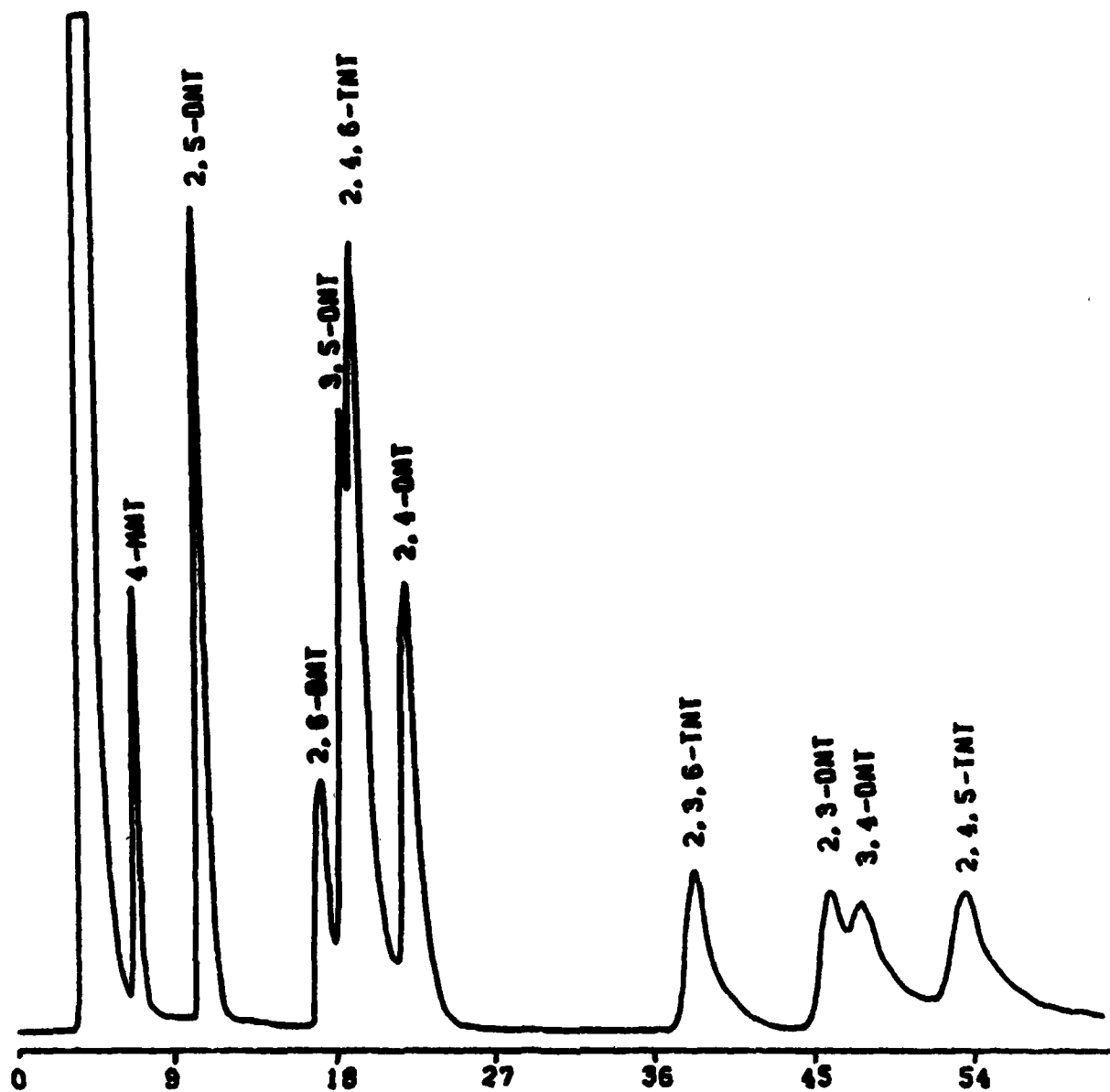


Figure 1

Retention volume ethyl acetate 2.5% in n-heptane at 3.0 ml/min.

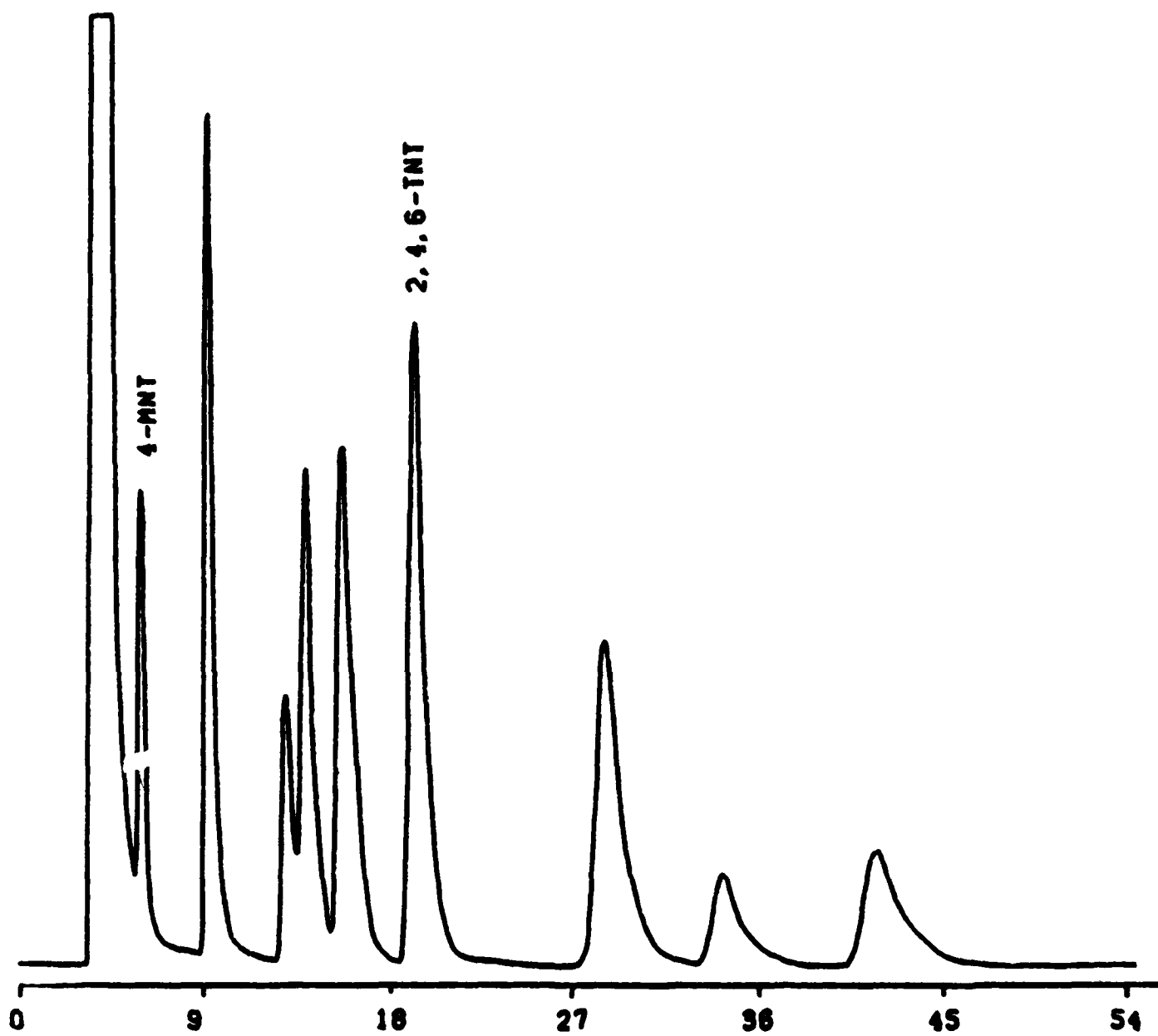


Figure 2

Retention volume propan-2-ol 0.25% in n-heptane at 3.0 ml/min.

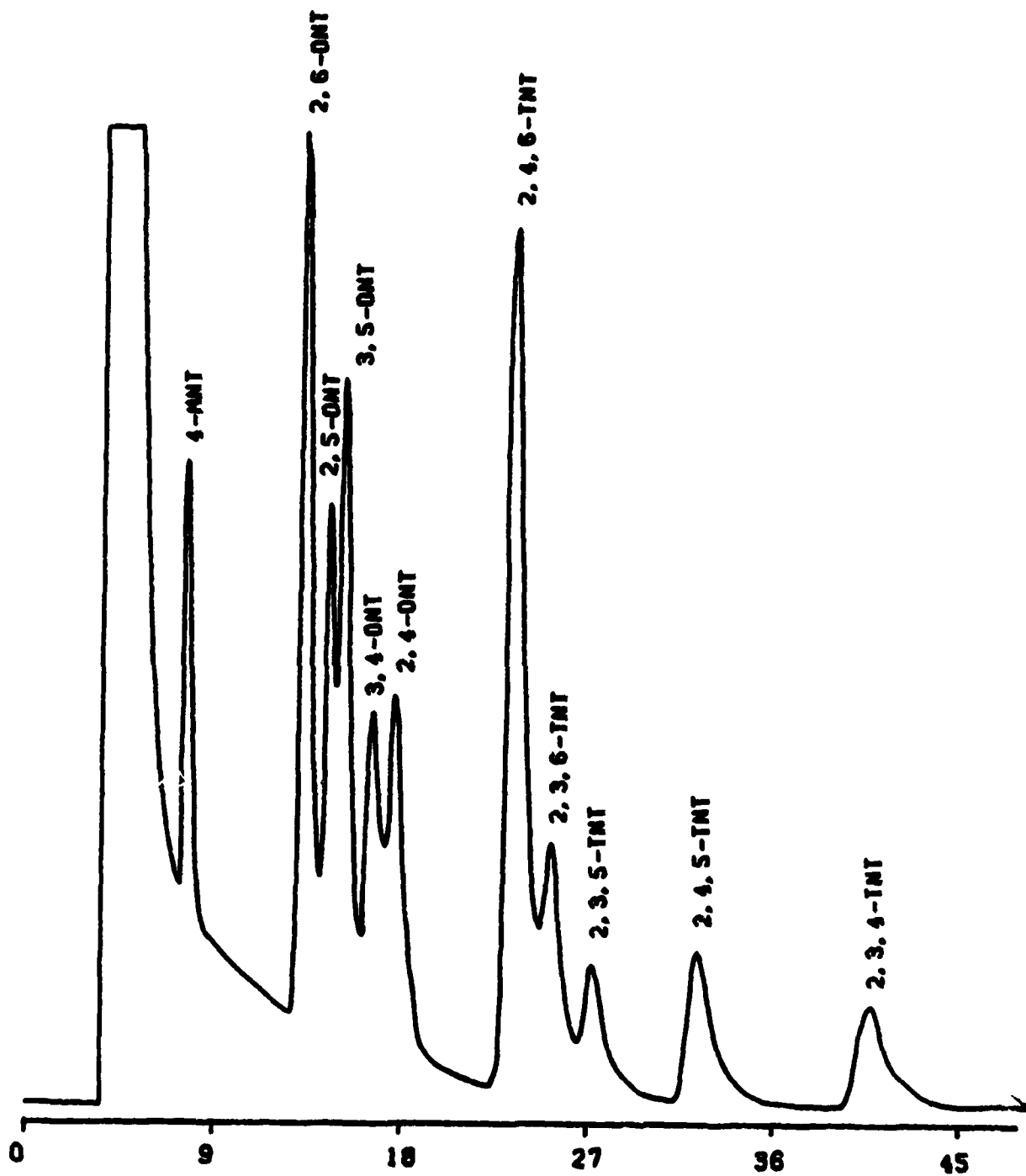


Figure 3

Retention volume dichloromethane 10% in n-heptane at 3.0 ml/min.

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